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Magnetic phase transitions in solid solutions of Fe-containing perovskite multiferoics

I.P. Raevski[1], S.P. Kubrin[1], A.V. Pushkarev[2], N.M. Olekhnovich[2], Y.V. Radyush[2], E.A. Bikyashev[3], S.I. Raevskaya[1],V.V. Titov[1], M.A. Malitskaya[1]

[1]*Research Institute of Physics and Faculty of Physics, Southern Federal University, 344090, Rostov-on-Don, Russia*
e-mail: igorraevsky@gmail.com

[2]*Scientific-Practical Materials Research Centre of NAS of Belarus, 220072, Minsk, Belarus*

[3]*Faculty of Chemistry, Southern Federal University, 344090, Rostov-on-Don, Russia*

One of the promising ways of designing new single-phase multiferroic materials is adjusting the temperatures of both ferroelectric and magnetic phase transitions by ion substitutions in the host compound to obtain the maximal magnetoelectric coupling. This presentation summarizes the results of the studies of the effect of ion substitutions in both A and B sublattices of the ABO_3 perovskite structure for several Fe-containing perovskite multiferroics: $BiFeO_3$, $PbFe_{0.5}Nb_{0.5}O_3$ (PFN) and $PbFe_{0.5}Sb_{0.5}O_3$ (PFS) on the temperatures of their magnetic phase transitions. All these perovskites exhibit antiferromagnetic ordering, however in both $BiFeO_3$ and PFN it is of G-type, while in PFS it is of I-type. Some solid solutions were synthesized in the perovskite structure for the first time using the high-pressure synthesis. Magnetic phase transition temperature T_M was determined by studying the Mössbauer spectra at different temperatures.

It is generally believed that in all perovskite ABO_3 multiferroics magnetic and ferroelectric subsystems are independent. Magnetic properties are provided by B-site (e.g. $Mn^{3+}$and Fe^{3+}) cations while ferroelectric properties are provided by the A-site cations having the so-called dangling bonds (Bi^{3+} and Pb^{2+}). In contrast to this assumption not only B-site but also A-site ion substitutions have been found to effect greatly the T_N value of PFN. In $BiFeO_3$- based solid solutions similar effects were also observed but only at high enough degree of the dilution of the Fe-sublattice. These results are explained using the models of magnetic superexchange involving the p-orbitals of Pb^{2+} or Bi^{3+} cations.

In the case of B-site substitutions theT_M values usually decrease with the concentration x of the substituting ion due to dilution of the magnetically active Fe-sublattice. At first T_M decreases rapidly as x grows (i.e. the Fe^{3+} concentration decreases), but then it saturates at $T_M \approx$ 40-50 K. This sharp change in the slope of $T_M(x)$ dependence roughly corresponds to the percolative phase transition from a long-range antiferromagnetic order to a short-range spin-glass one. Interestingly the Fe content at which the crossover between long-range and short-range magnetic ordering is approximately the same for all the substitutions studied, including magnetic and Mn^{3+} or Cr^{3+} ions. The results obtained imply that there is no magnetic exchange between Fe^{3+} and Cr^{3+} or Mn^{3+} ions. The reason of such behavior seems to be a difference in electronic configuration of Cr^{3+} (Mn^{3+}) and Fe^{3+} ions. Both Mn^{3+} and Cr^{3+} have a $t^3_{2g}e^1_g$ electronic configuration, while Fe^{3+} ion has a $t^3_{2g}e^2_g$ one. Thus, the value of transfer integral for 180° cation-anion-cation superexchange between octahedron-site $t^3_{2g}e^1_g$ and $t^3_{2g}e^2_g$ cations is close or equal to zero. The only difference between $T_M(x)$ dependences for nonmagnetic and magnetic substitutions for Fe^{3+} is that in the latter case the blocking temperature of the spin glass phase appears to be somewhat higher.

One more possibility to change the T_M values is to vary the ordering degree of B-cations in ternary $PbFe_{0.5}B^{5+}{}_{0.5}O_3$ perovskites, because such ordering changes dramatically the number of the magnetic neighbors around each Fe^{3+} ion. Such effects have been observed for some PFS-based solid solutions.

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